MITIGATION OF CRITICAL SINGLE POINT FAILURE (SPF) MATERIAL - Laminac 4116 BINDER REPLACEMENT PROGRAM for PARACHUTE and CLUSTER STARS ILLUMINANT COMPOSITIONS for HAND HELD SIGNALS

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ABSTRACT

Laminac 4116 binder has been identified as a single point failure (SPF) material since it is being produced by only one company and there is a possibility that the company may discontinue production due to low product demand. In addition, other issues involved with the use of Laminac include limited shelf life, environmental and health hazardous concerns. An investigation was conducted to develop alternate and environmentally compatible binder materials to replace Laminac in illuminant compositions for Hand Held Signals (HHS). Several vinyl alcohol acetate resins (VAAR) produced by different companies were investigated. Based on the static burn test results, vinyl alcohol acetate resins (by UC and McGean Inc. and 3V Inc. (trade name, Polivic-S202) were selected and optimized for illuminant compositions. Qualification tests for the full-up signals were conducted with the new binders in illuminant compositions at hot, ambient and cold temperatures per First Article Testing (FAT) protocol. This report discusses the test data and the evaluation criteria of the binders for hand held signals. The results indicate that the signals with the new binders met or exceeded the performance requirement and the data are comparable to the current Laminac signals. No critical failure was observed for any signal in the function tests conducted. Overall the data clearly demonstrated that both VAAR (by UC and McGean Inc.) and VAAR (by 3V Inc., Trade name Polivic S202) binder materials can be used to replace laminac 4116 binder in the illuminant compositions for HHS without compromising performance. This accomplishment has assured continued supply of reliable hand held signals (HHS) to our ground troop without interruption in the event of discontinued supply of Laminac 4116

1. INTRODUCTION

This effort is part of a broad-base program and mission directed by PEO AMMO Industrial Base office (PEO IB) and OPM-CCS to identify Single Point Failure (SPF) materials, issues and risks, potential impacts and mitigation actions. Laminac 4116 is used as a binder material in illuminant or first fire compositions for a good number of munitions and is being considered to be a **critical SPF Material.** It is produced by a single US source Ashland Specialty Chemical Inc. The producer finds that it is not economical to continue production due to limited commercial applications and unstable market. Other issues involved with the use of Laminac material include environmental and health hazardous concerns. Laminac is a polyester base resin that cross-links to a thermoset copolymer with a vinyl monomer, styrene. Lupersol DDM-9 serves as a catalyst for the polyester resin cross-linking and it contains methyl ethyl ketone peroxide (MEKP). Both styrene and MEKP are toxic materials and are extremely hazardous to health and environment. Load plants have complaints about these materials. Another drawback of Laminac is that it has a limited pot life when incorporated with the cure agent, forcing manufacturers to blend a mix and press it within a very short time. Based on the above concerns and issues, an investigation was conducted to identify suitable alternate and environmentally compatible binder materials for pyrotechnic compositions.

2. TECHNICAL APPROACH

Hand Held Signals (HHS) was chosen as the technology demonstration candidate for this program. HHS is used by ground troops to signal location and to communicate a distress situation. They can also be used to illuminate a small area for short periods of time. This particular family of signals (ref figs 1-2) consists of two types, Star Clusters (M125AI -Green Star, Ml58 -Red Star, and M159 - White Star) and Parachutes (M126Al - Red Star, M127Al -White Star, and the M195-Green Star). The illuminant charge compositions for HHS consist of magnesium fuel, various oxidizers and laminac 4116 binder. The overall thrust of this effort is to determine the use of alternate binder materials without compromising the performance characteristics of the signal systems. Vinyl alcohol acetate resins (VAAR) by different manufacturers were identified (Technical bulletins) for evaluation based on several criteria including environmental acceptability (toxicity characteristics), solubility in solvent, thermal stability, commercial availability, and compatibility with pyrotechnic ingredients (Chen et al.). These were

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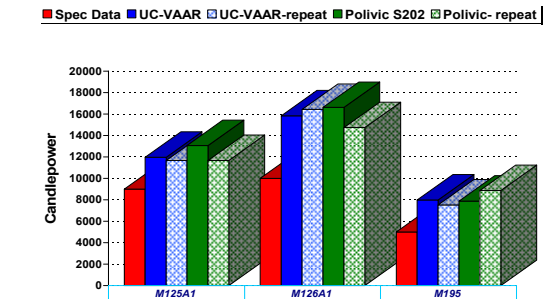
produced by UC/DOW (trade name Bakelite VAAR, MA-28-18, conforming to MIL -V-50443)), McGean Inc. (trade name McGean –VAAR, conforming to MIL-V-50443), 3V Inc. (resin trade name Polivic S202), and SYNTHOMER Inc. (resin trade name Alcotex B359) and polyvinyl acetate resin (trade name McGean PVA - B100). The binders except PVA-B100 (solid beads) were all viscous liquids of vinyl alcohol acetate resins with a slight difference in the degree of hydrolysis, solid contents, and physical properties (table 1). Static burn tests were performed (per military specifications, MIL-S-13257H and MIL-S-13261G) measuring candlepower (CP), burn time (BT), color characteristics ((%) purity and dominant wavelength (DW)) for each illumination candle with alternate binder materials. The composition of fuel, oxidizer and binder were adjusted in several iterations to optimize the candle outputs. Based on the test results two binders were down-selected and performed the first article testing (FAT) protocol procedures for over 1500 signal units to qualify two binders for the illuminant compositions. The preparation of illuminant candles, signals, static burn tests and function tests were conducted at Security Signal Inc. testing facility. Energetic material qualification (EMQ) sensitivity tests were also conducted to assure the safety of illuminant compositions with alternate binder materials.

3. RESULTS AND DISCUSSIONS

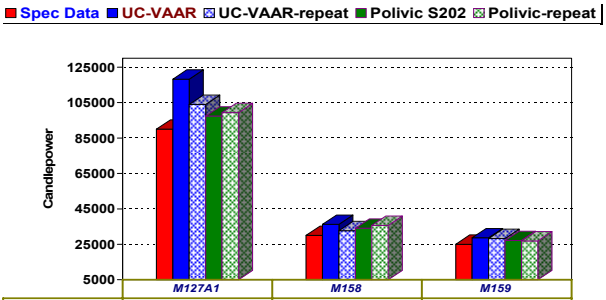
3.1 Static Burn Test Data:

More than fifteen hundred illuminant candles/star samples were tested over several iterations with UC-VAAR, McGean -VAAR, Polivic S202, Alcotex B359 or McGean PVA -B100 in illuminant compositions for all the signals to optimize the required performance (CP, BT, DW and percent (%) purity). Several iterations and tests were necessary for each signal to fine tune the composition to meet or exceed the performance requirement. Three binders (VAAR, Polivic S202 and PVA-B100) in illuminant candle composition for each signal met or exceeded the static burning performance requirements. The color characteristics (% purity and dominant wave length (DW)) for illuminant candles also met the required spec values for each signal. The results are all comparable to that of laminac binder in compositions. After the first iteration further tests were discontinued with Alcotex 359 B binder due to difficulties experienced in preparing homogeneous composition and consolidation. Moreover Alcotex B359B, being a foreign source, may present potential impediment for obtaining the binder. The results for candlepower and burn time for all signals are shown in figures 3-6. Two candidates had to be selected among the three successful binders. Since McGean PVA -B100 is available only as solid pellets, it has to be dissolved in a solvent (ethyl acetate) prior to use as a binder in illuminant compositions. It was also observed that the mixes using McGean PVA - B100 binder (ethyl acetate solvent) emitted very strong smelling vapors during the mixing process requiring the mix operator to wait for fumes to dissipate before removing the mix from the mixer. This would obviously increase cycle time for mixing as well. This procedure would require an extra step/process in the production environment with the associated additional cost and control; hence, McGean PVA - B100 binder was not selected. Both UC/ McGean -VAAR and Polivic S202 are available in liquid form and can be used readily to mixing/blending with the fuel and oxidizers to prepare illuminant mixes. UC-VAAR and McGean - VAAR meet Mil-V-50433 specification and either one of them can be used in the compositions. Based on the overall performance and processing improvement in the preparation of mixes, two binder candidates, VAAR and Polivic S202, were down-selected for engineering testing. The reproducibility results for static burn tests were good for all illuminant candles using VAAR and Polivic S202 in the compositions for M125A1, M126A1, M127A1, M195, M158 and M159 signals (ref figs 3-6).



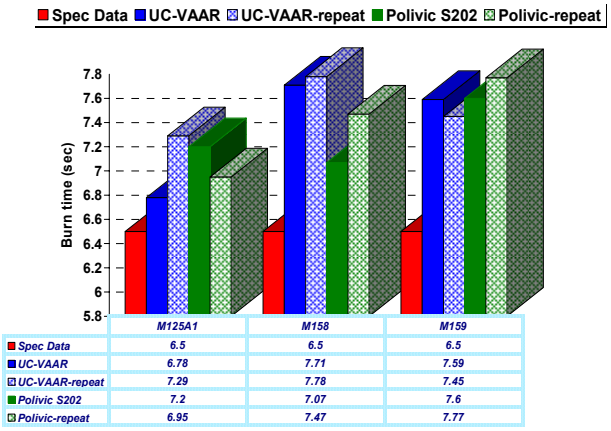
	M125A1	M126A1	M195
Spec Data	9000	10000	5000
UC-VAAR	11970	15838	7983
UC-VAAR-repeat	11662	16437	7515
Polivic S202	13051	16619	7873
Polivic- repeat	11675	14735	8861

Fig 3: Candlepower data for 125A1, 126A1 and M195



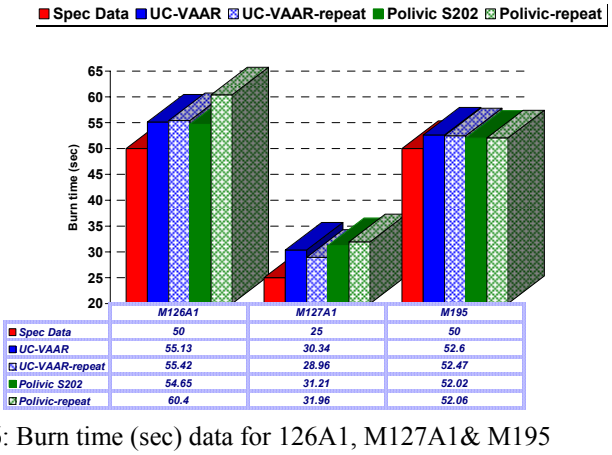
	M127A1	M158	M159
Spec Data	90000	30000	25000
UC-VAAR	118258	36203	28676
UC-VAAR-repeat	103946	32685	28239
Polivic S202	97387	34050	27131
Polivic-repeat	99399	35666	26880

Fig 4: Candlepower data for 127A1, M158 and M159



	M125A1	M158	M159
Spec Data	6.5	6.5	6.5
UC-VAAR	6.78	7.71	7.59
UC-VAAR-repeat	7.29	7.78	7.45
Polivic S202	7.2	7.07	7.6
Polivic-repeat	6.95	7.47	7.77

Fig 5: Burn time (sec) data for 125A1, M158 and M159

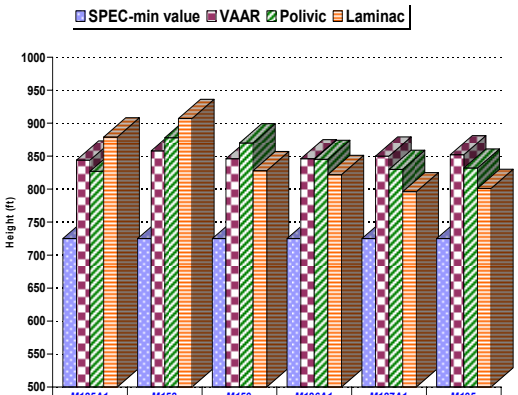


	M126A1	M127A1	M195
Spec Data	50	25	50
UC-VAAR	55.13	30.34	52.6
UC-VAAR-repeat	55.42	28.96	52.47
Polivic S202	54.65	31.21	52.02
Polivic-repeat	60.4	31.96	52.06

Fig 6: Burn time (sec) data for 126A1, M127A1& M195

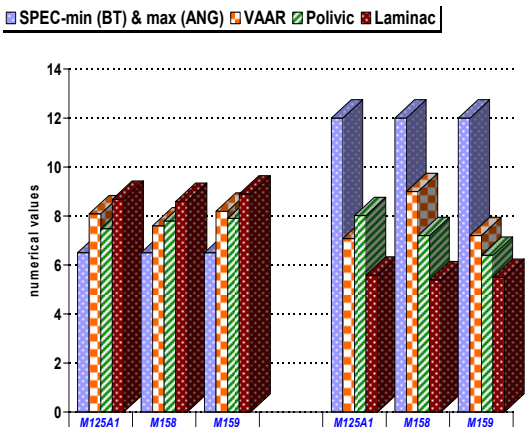
3. 2 Function Test:

Using the final successful illuminant compositions with VAAR and Polivic S202 binders the qualification tests were conducted per first article test (FAT) protocol (Mil-S-13257H/Mil-S-13261G). These include function tests for full-up signals at hot temperature (68°C-74°C) ambient temperature (18 °C-24° C) and cold temperature (-57°C to -51° C). Over nine hundred sixty cluster stars (M125A1 Green, M158 Red and M159 White) and parachute stars (M126A1 Red, M127A1 White and M195 Green) signal assemblies were tested (at hot, 32 units per signal, at ambient, 32 units per signal and at cold, 16 units per signal). The packed signals were conditioned at hot, at ambient or at cold temperature for a minimum of 16 hours prior to function testing. The performance of the signals was observed for compliance of specification requirements. Over all, there were no single failure in premature bursts, premature ejection, and launch delay. The function tests for all signals with VAAR or Polivic S202 binders in illuminant compositions at hot, ambient and cold conditions met or exceeded the performance requirements and the results are comparable to that of signals with Laminac binder in the illuminant composition (results for laminac signals were obtained from the recent production lot testing). The data at hot and cold conditions are recorded mainly for informational purposes. At hot condition it was necessary to make sure the motor won't blow out and no critical defect occurs either at hot and cold conditions. Basically the signals must perform the best at ambient condition. The results at ambient temperature for all signals are represented in figures 7-10. The average altitude (feet) for illuminant assemblies for all signals was higher by 16-18% with VAAR binder, higher by 14-21% with polivic binder and higher by 10-21% with laminac binder than the spec requirement (min 725 feet). The average burn time for illuminant assemblies was higher by 10-26% with VAAR binder, higher by 7-25% with polivic binder and higher by 5-37% with laminac binder than the spec requirement The average angle of deviation from the vertical for illuminant assemblies for all signals was lower by 25 -55% with VAAR binder, lower by 31-47% with polivic binder and lower by 45-59% with laminac binder than the spec requirement (average angle of deviation must be below 12 degree and lower values are better). There were no critical failures observed in any of the function tests and very few major defects/failures occurred. Over all, there were no premature bursts, no premature ejection, and no launch delay (signals exited within two seconds) for all signals. All the signals have met the acceptance criteria without any critical failure.



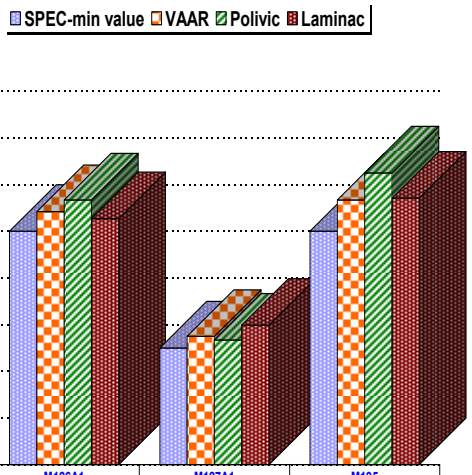
	M125A1	M158	M159	M126A1	M127A1	M195
SPEC-min value	725	725	725	725	725	725
VAAR	844	858	846	846	850	852
Polivic	827	878	870	845	830	832
Laminac	879	907	828	822	796	801

Fig 7: Altitude (feet) data for M125A1, M158, M159 M126A1, M127A1 and M195



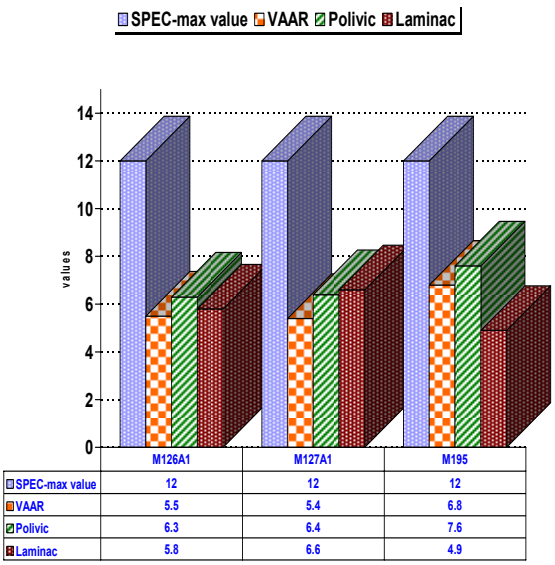
	M125A1	M158	M159		M125A1	M158	M159
SPEC-min (BT) & max (ANG)	6.5	6.5	6.5		12	12	12
VAAR	8.09	7.6	8.2		7.08	9	7.2
Polivic	7.49	7.8	7.9		8.02	7.2	6.4
Laminac	8.68	8.6	8.9		5.59	5.4	5.5

Fig 8: Burn time (sec) and Angle of Deviation (ANG) data for M125A1, M158 & M159



	M126A1	M127A1	M195
SPEC-min value	50	25	50
VAAR	54.2	27.5	56.7
Polivic	56.7	26.7	62.5
Laminac	52.7	29.9	57.1

Fig 9: Burn time (sec) data for M126A1, M127A1and M195



	M126A1	M127A1	M195
SPEC-max value	12	12	12
VAAR	5.5	5.4	6.8
Polivic	6.3	6.4	7.6
Laminac	5.8	6.6	4.9

Fig 10: Angle of deviation data for M126A1, M127A1and M195

3.3 Energetic material qualification (EMQ) tests:

The sensitivity tests were also conducted to assure the safety of illuminant compositions with alternate binder materials (Lakshminarayanan et al.). The test results indicated that the compositions exhibited thermally stability at 75°C and typical pyrotechnic burning characteristics without detonation or explosion. The compositions passed the electrostatic discharge (EDS), impact and friction tests (ref table 2).

4. CONCLUSIONS **

In summary both VAAR and Polivic S202 binders can be effectively used to substitute laminac 4116 binder in the illuminant compositions for hand held signals. VAAR can be considered as the *primary replacement candidate* and Polivic S202 can be considered as a *secondary replacement candidate*. It was observed that the preparation of mixes using Polivic S202 required an additional effort to clean the mixer after completing mixes due to its tendency to harden up in the mixer (particularly for M127A1 with sodium nitrate oxidizer in the composition). This would increase cycle time for mixing and therefore may reduce production capacity. VAAR is relatively easy to handle in the preparation of mixes. VAAR is very stable and has a long shelf life (over 10 years) and is a proven material for over fifty munitions. In addition, since it has already been used in delay compositions (part of the system) for all hand held signals, using VAAR in illuminant composition would be an added advantage. It has to be noted that although Dow Chemical Company has discontinued producing VAAR, the U.S. Army has bought unlimited rights for

VAAR manufacturing process and transferred the technology to McGean Inc. for production of VAAR (as a second source). Hence, in future, there will be continuous supply of VAAR (conforming to Mil-V-50443) from the second source. Polivic S202, which is also very stable material and has a good shelf life, can be obtained commercially for use as a binder. As far as processing the compositions after mixing, there is no noticeable difference between Laminac 4116, VAAR and Polivic S202. In summary, Laminac 4116 binder replacement program has been successfully completed to mitigate a critical single point failure material with two alternates (VAAR and Polivic 202) that are environmentally compatible and safe for use in illuminant compositions. This accomplishment has assured continued supply of reliable hand held signals (HHS) to our ground troop without interruption in the event of discontinued supply of Laminac 4116.

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Chen G, Lakshminarayanan G.R and Wejsa, J. Evaluation of alternate resin/binder materials to substitute vinyl alcohol acetate resin (VAAR) in pyrotechnic compositions, Technical Report ARWEC-TR-02007 (Dec 2002)

Lakshminarayanan, G.R., Chen, G, Lee Wai T and Giufurta, M, Energetic material qualification (EMQ) tests for illumination charge compositions with alternate binder materials for Hand held Signals Technical report ARAET-TR-05006 (May 2005) ; HCSDS-500; HCSDS - 2304

Technical Information Bulletins for "Bakelite Vinyl Alcohol Acetate Resin (VAAR) Solution, MA -28-18," Dow-Union Carbide Specialty Chemical Division, Danbury, CT; "McGean –VAAR, and PVA- B100," McGean Inc, Cleveland, OH; "Polivic S202"- 3V Inc. Plastic Additives Division, Weehawken, NJ ; "Alcotex 359B" Synthomer Limited, Central Road, Temple Fields, Harlow, Essex, CM20 2BH, UK and distributed by Focus Chemical Corp., Portsmouth, NH

** *The materials used in this program and the views and conclusions contained in this paper are those of the authors and should not be interpreted as representing the official policies, either expressed or implied of ARDEC or the U.S. Government*

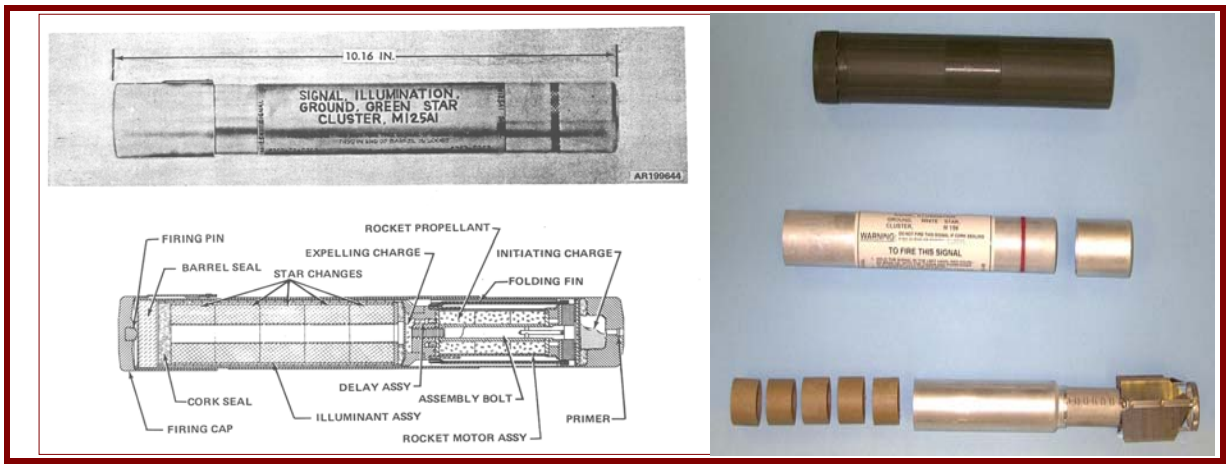

Figure 1: SIGNALS, ILLUMINATION, GROUND, CLUSTERS, GREEN STAR, M125A1; RED STAR, M158; WHITE STAR, M159: For daytime or night time signaling

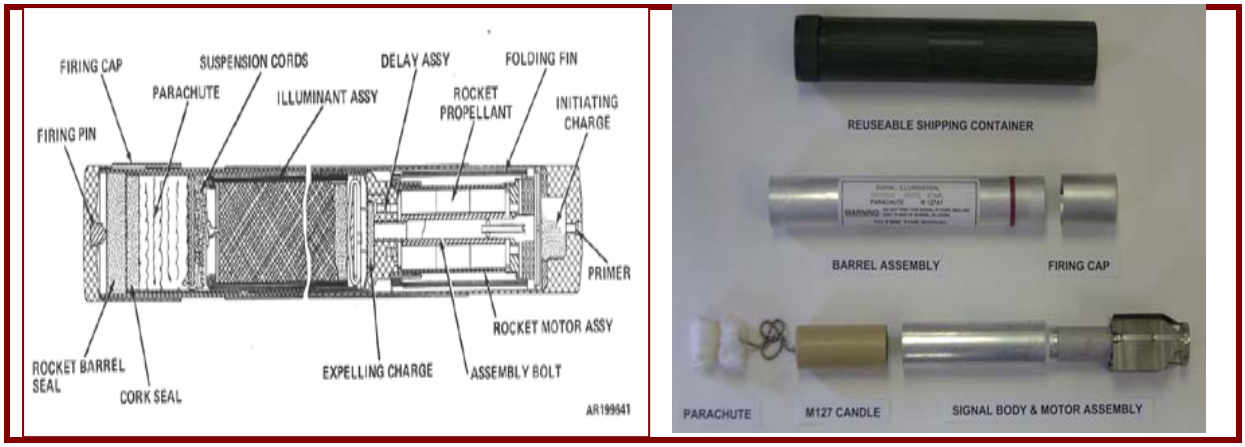

Figure 2: SIGNALS, ILLUMINATION, GROUND: PARACHUTES, RED STAR, M126A1; WHITE STAR, M127A1; AND GREEN STAR, M195: For daytime and night time signaling and night time illumination in the case of the M127A1

Table 1: Resin Properties–Data from Company Tech Bulletins and Data from SGS US Testing Laboratory

Binder/Resin	Solvent for Resin	Appearance	Color (cpu) (Mil-V-50433) Cobalt Platinum Method		% by weight dry resin basis (Alcohol Content)			% Solids Mil-V-50433	
					(Mil-V-50433)		ASTM D-1396		
			Company data	SGS data	Company Data	SGS data	SGS data	Company data	SGS data
UC-VAAR (30mol % VAAR) (Bakelite MA-28-18)	Methanol (82%) + Methyl acetate (18%)	Clear	300 max	150 -200	16-19	17.5	10.3	26 -29	30.3
McGean -VAAR[b]	Methanol (82%) + Methyl acetate (18%)	Clear	100	-	17.5	-	-	27.6	-
Polyvic S202-35% (Degree of hydrolysis 47mol %)	Methanol (100%)	Brown yellow liquid		100 -150	30-32	31.0	22.0	35	35.8
Alcotex 359B (Degree of hydrolysis 33-40 mol %)	Methanol (90%) + Methyl acetate (10%)	Water white to pale straw/clear Slight haze	---	40-60	20-26	22.5	18.0	25– 27	26.7
McGean PVA- B100	Not applicable	Beads	Colorless/ Straw Yellow beads		Not applicable			Not applicable	
Laminac 4116[C]	Lupersol DDM9	Amber liquid Styrene odor			Polyester resin 61.0-66.0 Styrene 36			Acid value (solid basis) 32.1 unit	

[a] SGS U.S. Testing Laboratory (75 Passaic Ave, Fairfield, NJ 07004) performed the tests
[b] McGean -VAAR, second source production of VAAR per MI-V-50433, dated November 2005 (lots 40379409 and 40379411)
[c] Source for Laminac 4116 from company technical bulletin, Ashland Specialty Chemical Company, PO Box: 2219, Columbus, OH

Table 2: Summary of EMQ Tests for Illuminant Charges with different binders for Hand Held Signals

EMQ Tests	Laminac or VAAR * or Polivic or Alcotex or McGean B-100 binder in Illuminanant Compositions for Signals						
	M125A1	**M126A1**	**M127A1**	**M195**	**M158**	**M159**	Remarks
DSC profile at 5C/min heating rate	Exotherm Peaks	Exotherm/ Enodotherm Peaks	Enodotherm Peaks	Enodotherm Peaks	Exotherm/ Peaks	Exotherm/ Enodotherm Peaks	Observed normal Exotherm (detonation or deflagration) and/ or Enodotherm (melting)
Vacuum Stability at 100C/40 Hours	Pass – Stable	Pass – Stable	Pass – Stable	Pass – Stable	Pass – Stable	Pass – Stable	Minimal gas liberation (far less than the acceptable max of 3 ml at STP)
Thermal Stability at 75C/48 Hours	Pass – Stable	Pass – Stable	Pass – Stable	Pass – Stable	Pass – Stable	Pass – Stable	Minimal loss of weight (less than 0.75% due to moisture) Acceptable
Small scale Burn test	Pass	Pass	Pass	Pass	Pass	Pass	No detonation or explosion
Ignition -5 sec explosive temp	Pass - No reaction	Pass -No reaction	Pass - No reaction	Pass - No reaction	Pass - No reaction	Pass - No reaction	Pass- no reaction (flame or audible report) in test trials up to 500C
Electrostatic Sensitivity	Pass - No reaction	Pass -No reaction	Pass -No reaction	Pass -No reaction	Pass - No reaction	Pass - No reaction	Pass- no reaction (flash, spark, burn or noise) in 20 trials at 0.25 joule
ERL/Bruceton Impact test	Pass	Pass	Pass	Pass	Pass	Pass	All mixes are impact insensitive
BOE - Impact Sensitivity	Pass	Pass	Pass	Pass	Pass	Pass	All mixes are impact insensitive
ABL-Friction Sensitivity	All signals pass ABL- friction test (no reaction (flash, spark, burn or cracking) at a Min force value of 4450N & mostly at 8000N; with VAAR binder the values are slightly lower; Refer -HCSDS for EMQ test information: M195-HCSDS no. 2304; M158-HCSDS no.500 and M159-HCSDS no. 501						
BAM Friction Sensitivity	All signals pass BAM friction test - no reaction (flash, spark, burn or cracking) at a Min force value of 324N & mostly at 360N; with VAAR binder the values are lower; Refer -HCSDS for EMQ test information: M195-HCSDS no. 2304; M158-HCSDS no.500 and M159-HCSDS no. 501						